

APPENDIX

5 Molecules evidencing one of several new types of switching are provided for the colorant layer 101. That is to say, the present invention introduces several new types of switching mechanisms that distinguish it from the prior art:

(1) an electric field ("E-field") induced rotation of at least one rotatable section (rotor) or a molecule to change the band gap of the molecule;

(2) E-field induced charge separation or recombination of the molecule via chemical bonding change to change the band gap; and

10 (3) E-field induced band gap change via molecular folding or stretching.

Thus, the color switching is the result of an E-field induced intramolecular change rather than a diffusion or oxidation/reduction reaction, in contrast to prior art approaches. Also, the part of the molecule that moves is quite small, so the switching time is expected to be quite fast. Also, the molecules are much simpler and thus easier and cheaper to make than the rotaxanes, catenanes, and related compounds.

15 The following are examples of model molecules with a brief description of their function:

(1) E-field induced band gap change via molecular conformation change (rotor/stator type of model) - FIGS. 4 and 5a-5c;

20 (2a) E-field-induced band gap change caused by the change of extended conjugation via charge separation or recombination accompanied by increasing or decreasing band localization - FIG. 6a;

(2b) E-field-induced band gap change caused by change of extended conjugation via charge separation or recombination and π -bond breaking or formation - FIG. 6b; and

25 (3) E-field-induced band gap change via molecule folding or stretching - FIG. 7.

Each model, with supporting examples, is discussed below. However, the examples given are not to be considered limiting the invention to the specific molecular systems illustrated, but rather merely exemplary of the above switching mechanisms.

30

Model (1): E-Field-Induced Band Gap Change Via Molecular Conformation Change (Rotor/Stator Type of Model):

FIG. 4 is a schematic depiction of one embodiment of this model, which involves an E-field-induced band gap change via molecular conformation change (rotor/stator type of model). As shown in FIG. 4, the molecule 430 comprises a rotor portion 432 and a stator portion 434. The rotor portion 432 rotates with an applied electric field. In one state, depicted on the left side of the drawing, there is an extended conjugation through the entire molecule, resulting in a relatively smaller band gap and thereby longer wavelength (red-shifted) photo-absorption. In the other state, following rotation of the rotor, depicted on the right side of the drawing, the extended conjugation is destroyed, resulting in a relatively larger band gap and thereby shorter wavelength (blue-shifted) photo-absorption. FIGS. 5a-5c depict an alternate, and preferred, embodiment of this Model 1; these latter Figures are discussed in connection with Examples 1 and 2 of this Model 1 below.

The following requirements must be met in this model:

- (a) The molecule must have at least one rotor segment and at least one stator segment;
- (b) In one state of the molecule, there should be delocalized HOMOs and/or LUMOs (π -states and/or non-bonding orbitals) that extend over a large portion of the molecule (rotor(s) and stator(s)), whereas in the other state, the orbitals are localized on the rotor(s) and stator(s), and other segments;
- (c) The connecting unit between rotor and stator can be a single σ -bond or at least one atom with (1) non-bonding electrons (p or other electrons), or (2) π -electrons, or (3) π -electrons and non-bonding electron(s);
- (d) The non-bonding electrons, or π -electrons, or π -electrons and non-bonding electron(s) of the rotor(s) and stator(s) can be localized or de-localized depending on the conformation of the molecule, while the rotor rotates when activated by an E-field;
- (e) The conformation(s) of the molecule can be E-field dependent or bi-stable;

(f) The bi-stable state(s) can be achieved by intra- or inter-molecular forces such as hydrogen bonding, Coulomb force, van der Waals force, metal ion complex or dipole inter-stabilization; and

(g) The band gap of the molecule will change depending on the degree of non-bonding electron, or π -electron, or π -electron and non-bonding electron delocalization of the molecule. This will control the optical properties (e.g., color and/or index of refraction, etc.) of the molecule.

Following are two examples of this model (Examples 1 and 2):

The novel bi-modal molecules of the present invention are active optical devices that can be switched with an external electric field. Preferably, the colorant molecules are bi-stable. The general idea is to design into the molecules a rotatable middle segment (rotor) 432 that has a large dipole moment (see Examples 1 and 2) and that links two other portions of the molecule 430 that are immobilized (stators) 434. Under the influence of an applied electric field, the vector dipole moment of the rotor 432 will attempt to align parallel to the direction of the external field. However, the molecule 430 is designed such that there are inter- and/or intra-molecular forces, such as hydrogen bonding or dipole-dipole interactions as well as steric repulsions, that stabilize the rotor 432 in particular orientations with respect to the stators 434. Thus, a large electric field is required to cause the rotor 432 to unlatch from its initial orientation and rotate with respect to the stators 434.

Once switched into a particular orientation, the molecule 430 will remain in that orientation until it is switched to a different orientation, or reconfigured. However, a key component of the molecule design is that there is a steric repulsion or hindrance that will prevent the rotor 432 from rotating through a complete 180 degree half cycle. Instead, the rotation is halted by the steric interaction of bulky groups on the rotor 432 and stators 434 at an optically significant angle of typically between 10° and 170° from the initial orientation. For the purposes of illustration, this angle is shown as 90° in the present application. Furthermore, this switching orientation may be stabilized by a different set of inter- and/or intra-molecular hydrogen bonds or dipole interactions, and is thus latched in place even after the applied field is turned off. For bi- or multi- stable colorant molecules, this ability to latch the rotor 432 between two states separated by an optically significant rotation from the stators is crucial.

The foregoing strategy may be generalized to design colorant molecules to provide several switching steps so as to allow multiple states (more than two) to produce a multi-state (e.g., multi-color) system. Such molecules permit the optical properties of the colorant layer to be tuned continuously with a decreasing or increasing electric field, or changed abruptly from one state to another by applying a pulsed field.

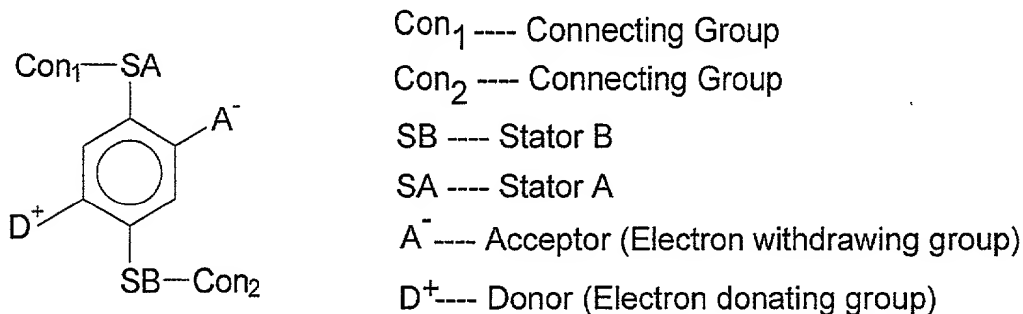
Further, the colorant molecules may be designed to include the case of no, or low, activation barrier for fast but volatile switching. In this latter situation, bi-stability is not required, and the molecule is switched into one state by the electric field and relaxes back into its original state upon removal of the field ("bi-modal"). In effect, these forms of the bi-modal colorant molecules are "self-erasing". In contrast, with bi-stable colorant molecules, the colorant molecule remains latched in its state upon removal of the field (non-volatile switch), and the presence of the activation barrier in that case requires application of an opposite field to switch the molecule back to its previous state.

When the rotor 432 and stators 434 are all co-planar, the molecule is referred to as "more-conjugated". Thus, the non-bonding electrons, or π -electrons, or π -electrons and non-bonding electrons of the colorant molecule, through its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are delocalized over a large portion of the molecule 430. This is referred to as a "red-shifted state" for the molecule, or "optical state I". In the case where the rotor 432 is rotated out of conjugation by approximately 90° with respect to the stators 434, the conjugation of the molecule 430 is broken and the HOMO and LUMO are localized over smaller portions of the molecule, referred to as "less-conjugated". This is a "blue-shifted state" of the molecule 430, or "optical state II". Thus, the colorant molecule 430 is reversibly switchable between two different optical states.

It will be appreciated by those skilled in the art that in the ideal case, when the rotor 432 and stators 434 are completely coplanar, then the molecule is fully conjugated, and when the rotor 432 is rotated at an angle of 90° with respect to the stators 434, then the molecule is non-conjugated. However, due to thermal fluctuations, these ideal states are not fully realized, and the molecule is thus referred to as being "more-conjugated" in the former case and "less-conjugated" in the latter case. Further, the terms "red-shifted" and "blue-shifted" are not meant to convey any relationship to

hue, but rather the direction in the electromagnetic energy spectrum of the energy shift of the gap between the HOMO and LUMO states.

Examples 1 and 2 show two different orientations for switching the molecules. Example 1a below depicts a first generic molecular example for this Model 1.



Example 1a

where:

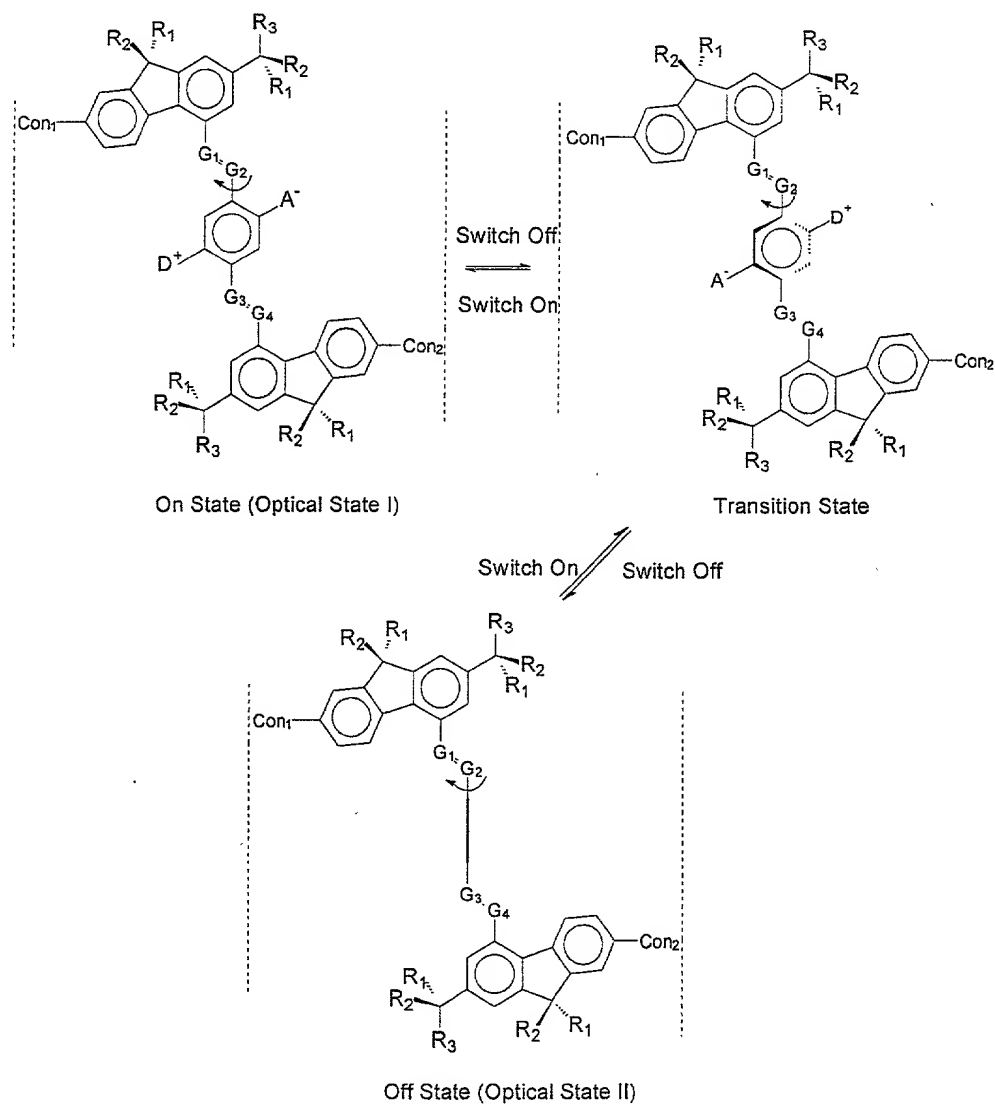
The letter A⁻ represents an Acceptor group; it is an electron-withdrawing group. It may be one of the following: hydrogen, carboxylic acid or its derivatives, sulfuric acid or its derivatives, phosphoric acid or its derivatives, nitro, nitrile, hetero atoms (e.g., N, O, S, P, F, Cl, Br), or functional groups with at least one of above-mentioned hetero atoms (e.g., OH, SH, NH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

The letter D⁺ represents a Donor group; it is an electron-donating group. It may be one of following: hydrogen, amine, OH, SH, ether, hydrocarbon (either saturated or unsaturated), or substituted hydrocarbon or functional group with at least one of hetero atom (e.g., B, Si, I, N, O, S, P). The donor is differentiated from the acceptor by that fact that it is less electronegative, or more electropositive, than the acceptor group on the molecule.

The letters Con₁ and Con₂ represent connecting units between one molecule and another molecule or between a molecule and the solid substrate (e.g., metal electrode, inorganic or organic substrate, etc.). They may be any one of the following: hydrogen (utilizing a hydrogen bond), multivalent hetero atoms (i.e., C, N, O, S, P, etc.) or functional groups containing these hetero atoms (e.g., NH, PH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

The letters SA and SB are used here to designate Stator A and Stator B. They may be a hydrocarbon (either unsaturated or saturated) or substituted hydrocarbon. Typically, these hydrocarbon units contain conjugated rings that contribute to the extended conjugation of the molecule when it is in a planar state (red shifted state). In those stator units, they may contain the bridging group G_n and/or the spacing group R_n . The bridging group (e.g., acetylene, ethylene, amide, imide, imine, azo, etc.) is typically used to connect the stator to the rotor or to connect two or more conjugated rings to achieve a desired chromophore. The connector may alternately comprise a single atom bridge, such as an ether bridge with an oxygen atom, or a direct sigma bond between the rotor and stator. The spacing groups (e.g., phenyl, isopropyl or tert-butyl, etc.) are used to provide an appropriate 3-dimensional scaffolding to allow the molecules to pack together while providing space for each rotor to rotate over the desired range of motion.

Example 1b below is a real molecular example of Model 1. In Example 1b, the rotation axis of the rotor is designed to be nearly perpendicular to the net current-carrying axis of the molecules, whereas in Example 2, the rotation axis is parallel to the orientation axis of the molecule. These designs allow different geometries of molecular films and electrodes to be used, depending on the desired results.



where:

The letter A⁻ is an Acceptor group; it is an electron-withdrawing group. It may be one of following: hydrogen, carboxylic acid or its derivatives, sulfuric acid or its derivatives, phosphoric acid or its derivatives, nitro, nitrile, hetero atoms (e.g., N, O, S, P, F, Cl, Br), or functional group with at least one of above-mentioned hetero atoms (e.g., OH, SH, NH, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

The letter D⁺ represents a Donor group; it is an electron-donating group. It may be one of following: hydrogen, amine, OH, SH, ether, hydrocarbon (either saturated or unsaturated), or substituted hydrocarbon or functional group with at least one of hetero atom (e.g., B, Si, I, N, O, S, P). The donor is differentiated from the acceptor by that fact that it is less electronegative, or more electropositive, than the acceptor group on the molecule.

The letters Con₁ and Con₂ represent connecting units between one molecule and another molecule or between a molecule and the solid substrate (e.g. metal electrode, inorganic or organic substrate, etc.). They may be any one of the following: hydrogen (utilizing a hydrogen bond), multivalent hetero atoms (i.e., C, N, O, S, P, etc.) or functional groups containing these hetero atoms (e.g., NH, PH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

Letters R₁, R₂, R₃ represent spacing groups built into the molecule. The function of these spacer units is to provide an appropriate 3-dimensional scaffolding to allow the molecules to pack together while providing rotational space for each rotor. They may be any one of the following: hydrogen, hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

Letters G₁, G₂, G₃, and G₄ are bridging groups. The function of these bridging groups is to connect the stator and rotor or to connect two or more conjugated rings to achieve a desired chromophore. They may be any one of the following: hetero atoms (e.g., N, O, S, P, etc.) or functional groups with at least one of above-mentioned hetero atoms (e.g., NH or NHNH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons. The connector may alternately comprise a single atom bridge such as an ether bridge with an oxygen atom, or a direct sigma bond between the rotor and stator.

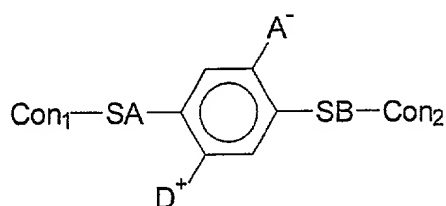
In Example 1b above, the vertical dotted lines represent other molecules or solid substrates. The direction of the switching field is perpendicular to the vertical dotted lines. Such a configuration is employed for electrical switching; for optical switching, the linking moieties may be eliminated, and the molecule may be simply placed between the two electrodes. They may also be simply used to link one molecule to another molecule or a molecule to an organic or inorganic solid substrate.

Referring to FIG. 5a, the molecule shown above (Example 1b) has been designed with the internal rotor 432 perpendicular to the orientation axis of the entire molecule 430. In this case, the external field is applied along the orientation axis of the molecule 430 as pictured - the electrodes (vertical dotted lines) are oriented perpendicular to the plane of the paper and perpendicular to the orientation axis of the molecule 430. Application of an electric field oriented from left to right in the diagrams will cause the rotor 432 as pictured in the upper diagram to rotate to the position shown on the lower right diagram, and vice versa. In this case, the rotor 432 as pictured in the lower right diagram is not coplanar with the rest of the molecule, so this is the blue-shifted optical state of the molecule, whereas the rotor is coplanar with the rest of the molecule on the upper diagram, so this is the red-shifted optical state of the molecule. The structure shown in the lower left diagram depicts the transition state of rotation between the upper diagram (co-planar, conjugated) and the lower right diagram (central portion rotated, non-conjugated).

The molecule depicted in Example 1b is chromatically transparent or blue-shifted. In the conjugated state, the molecule is colored or is red-shifted.

For the molecules in Example 1b, a single monolayer molecular film is grown, for example using Langmuir-Blodgett techniques or self-assembled monolayers, such that the orientation axis of the molecules is perpendicular to the plane of the electrodes used to switch the molecules. Electrodes may be deposited in the manner described by Collier et al, supra, or methods described in the above-referenced patent applications and issued patent. Alternate thicker film deposition techniques include vapor phase deposition, contact or ink-jet printing, or silk screening.

Example 2a below depicts a second generic molecular example for this Model 1.



Con₁ ---- Connecting Group

Con₂ ---- Connecting Group

SB ---- Stator B

SA ---- Stator A

A⁻ ---- Acceptor (Electron withdrawing group)

D⁺ ---- Donor (Electron donating group)

Example 2a

5 where:

The letter A⁻ is an Acceptor group; it is an electron-withdrawing group. It may be one of following: hydrogen, carboxylic acid or its derivatives, sulfuric acid or its derivatives, phosphoric acid or its derivatives, nitro, nitrile, hetero atoms (e.g., N, O, S, P, F, Cl, Br), or functional group with at least one of above-mentioned hetero atoms (e.g., OH, SH, NH, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

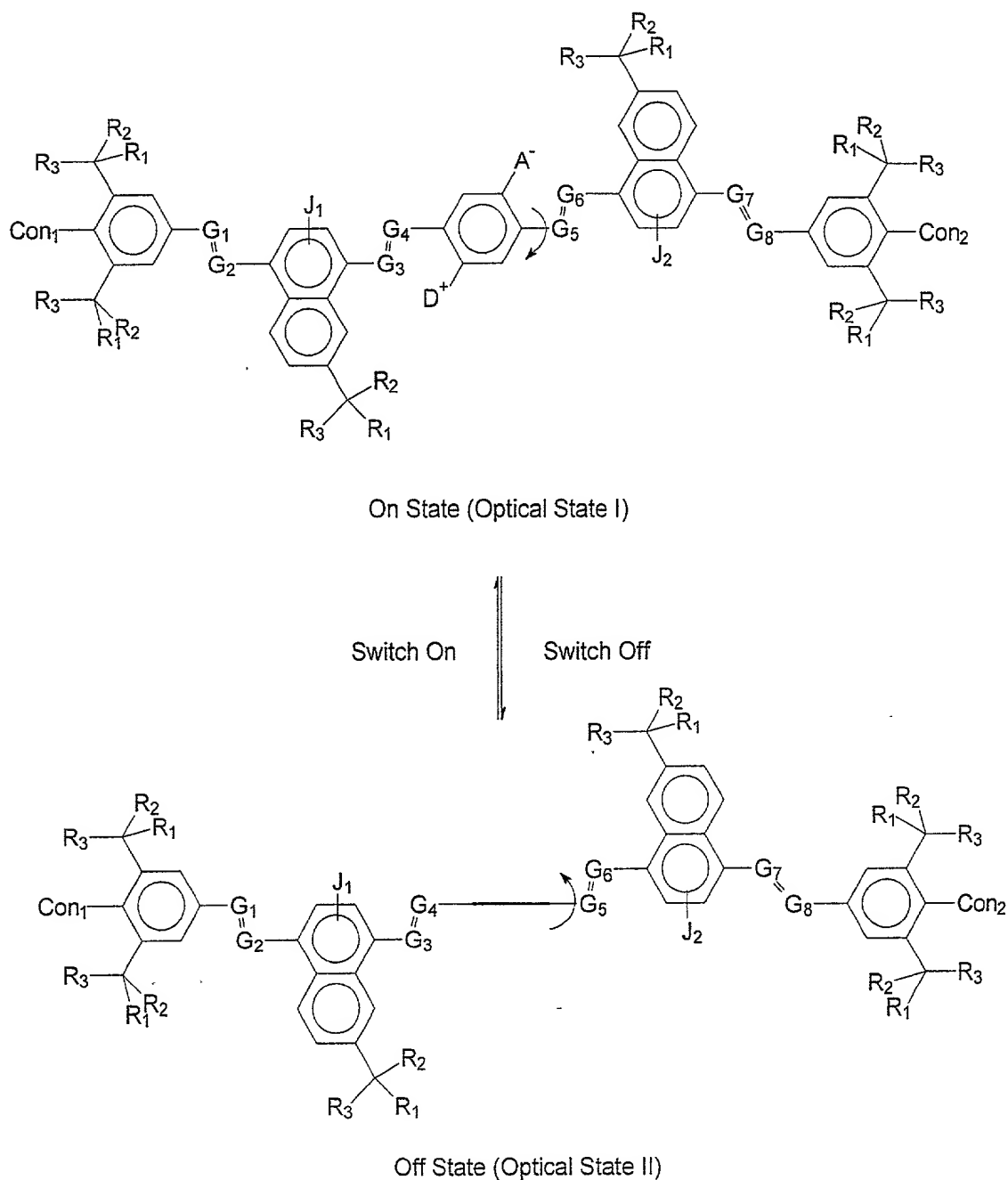
The letter D⁺ represents a Donor group; it is an electron-donating group. It may be one of following: hydrogen, amine, OH, SH, ether, hydrocarbon (either saturated or unsaturated), or substituted hydrocarbon or functional group with at least one of hetero atom (e.g., B, Si, I, N, O, S, P). The donor is differentiated from the acceptor by that fact that it is less electronegative, or more electropositive, than the acceptor group on the molecule.

The letters Con₁ and Con₂ represent connecting units between one molecule and another molecule or between a molecule and the solid substrate (e.g., metal electrode, inorganic or organic substrate, etc.). They may be any one of the following: hydrogen (utilizing a hydrogen bond), multivalent hetero atoms (i.e., C, N, O, S, P, etc.) or functional groups containing these hetero atoms (e.g., NH, PH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

The letters SA and SB are used here to designate Stator A and Stator B. They can be a hydrocarbon (either unsaturated or saturated) or substituted hydrocarbon. Typically, these hydrocarbon units contain conjugated rings that contribute to the extended conjugation of the molecule when it is in a planar state (red shifted state). In those stator units, they may contain bridging groups G_n and/or spacing groups R_n. A

bridging group is typically used to connect the stator and rotor or to connect two or more conjugated rings to achieve a desired chromophore. The connector may alternatively comprise a single atom bridge, such as an ether bridge with an oxygen atom, or a direct sigma bond between the rotor and stator. A spacing group provides an appropriate 3-dimensional scaffolding to allow the molecules to pack together while providing rotational space for each rotor.

Example 2b below is another real molecular example of Model 1.



Example 2b

where:

5 The letter A⁻ is an Acceptor group; it is an electron-withdrawing group. It may be one of following: hydrogen, carboxylic acid or its derivatives, sulfuric acid or its derivatives, phosphoric acid or its derivatives, nitro, nitrile, hetero atoms (e.g., N, O, S, P, F, Cl, Br), or functional group with at least one of above-mentioned hetero atoms (e.g., OH, SH, NH, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

10 The letter D⁺ represents a Donor group; it is an electron-donating group. It may be one of following: hydrogen, amine, OH, SH, ether, hydrocarbon (either saturated or unsaturated), or substituted hydrocarbon or functional group with at least one of hetero atom (e.g., B, Si, I, N, O, S, P). The donor is differentiated from the acceptor by that fact that it is less electronegative, or more electropositive, than the acceptor group on the molecule.

15 The letters Con₁ and Con₂ represent connecting units between one molecule and another molecule or between a molecule and the solid substrate (e.g., metal electrode, inorganic or organic substrate, etc.). They may be any one of the following: hydrogen (utilizing a hydrogen bond), multivalent hetero atoms (i.e., C, N, O, S, P, etc.) or functional groups containing these hetero atoms (e.g., NH, PH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

20 The letters R₁, R₂ and R₃ represent spacing groups built into the molecule. The function of these spacer units is to provide an appropriate 3-dimensional scaffolding to allow the molecules to pack together while providing rotational space for each rotor. They may be any one of the following: hydrogen, hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

25 The letters G₁, G₂, G₃, G₄, G₅, G₆, G₇, and G₈ are bridging groups. The function of these bridging groups is to connect the stator and rotor or to connect two or more conjugated rings to achieve a desired chromophore. They may be any one of the following: hetero atoms (e.g., C, N, O, S, P, etc.) or functional group with at least one of above-mentioned hetero atoms (e.g., NH or NHNH, etc.), hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons. The connector may alternately

comprise a single atom bridge such as an ether bridge with an oxygen atom, or a direct sigma bond between the rotor and stator.

The letters J₁ and J₂ represent tuning groups built into the molecule. The function of these tuning groups (e.g., OH, NHR, COOH, CN, nitro, etc.) is to provide an appropriate functional effect (e.g. both inductive effect and resonance effects) and/or steric effects. The functional effect is to tune the band gap ($\Delta E_{\text{HOMO/LUMO}}$) of the molecule to get the desired electronic as well as optical properties of the molecule. The steric effect is to tune the molecular conformation through steric hindrance, inter- or intra-molecular interaction forces (e.g. hydrogen bonding, Coulomb interaction, van der Waals forces) or to provide bi- or multiple-stability of molecular orientations. They may be any one of the following: hydrogen, hetero atoms (e.g., N, O, S, P, B, F, Cl, Br, and I), functional groups with at least one of above-mentioned hetero atoms, hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

The molecule shown above (Example 2b) has been designed with the internal rotor parallel to the orientation axis of the entire molecule. In this case, the external field is applied perpendicular to the molecular axis - the electrodes are oriented parallel to the long axis of the molecule and can be either nominally perpendicular or parallel to the plane of the above model structures. For example, application of an electric field to the upper molecule shown above where the field lines are perpendicular to the molecular axis and pointing upward will cause the rotor as pictured in that diagram to rotate to approximately 90 degrees and appear edge on, as shown in the lower molecular diagram above, and vice versa. In this case, the rotor as pictured in the lower diagram is not coplanar with the rest of the molecule, so this is the blue-shifted optical state of the molecule, or optical state II, whereas the rotor is coplanar with the rest of the molecule on the upper diagram, so this is the red-shifted optical state of the molecule, or optical state I. The letters N, H, and O retain their usual meaning.).

FIG. 5a depicts molecules similar to those of Examples 1b and 2b, but simpler, comprising a middle rotor portion 432 and two end stator portions 434. As in Examples 1b and 2b, the rotor portion 432 comprises a benzene ring that is provided with substituents that render the rotor with a dipole. The two stator portions 434 are each

covalently bonded to the benzene ring through an azo linkage, and both portions comprise an aromatic ring.

FIG. 5b is a schematic representation (perspective), illustrating the planar state, with the rotor 432 and stators 434 all co-planar. In the planar state, the molecule 430 is fully conjugated, evidences color (first spectral or optical state), and is comparatively more electrically conductive. The conjugation of the rings is illustrated by the π -orbital clouds 500a, 500b above and below, respectively, the plane of the molecule 430.

FIG. 5c is also a schematic representation (perspective), illustrating the rotated state, with the rotor 432 rotated 90° with respect to the stators 434, which remain co-planar. In the rotated state, the conjugation of the molecule 430 is broken. Consequently, the molecule 430 is transparent (second spectral or optical state) and comparatively less electrically conductive.

For the molecules of Example 2b, the films are constructed such that the molecular axis is parallel to the plane of the electrodes. This may involve films that are multiple monolayers thick. The molecules form solid-state or liquid crystals in which the large stator groups are locked into position by intermolecular interactions or direct bonding to a support structure, but the rotor is small enough to move within the lattice of the molecules. This type of structure can be used to build an E-field controlled display or used for other applications as mentioned earlier herein.

Model (2a): E-Field Induced Band Gap Change Caused by the Change of Extended Conjugation via Charge Separation or Recombination Accompanied by Increasing or Decreasing Band Localization:

FIG. 6a is a schematic depiction of this model, which involves an E-field-induced band gap change caused by the change of extended conjugation via charge separation or recombination accompanied by increasing or decreasing band localization. As shown in FIG. 6a, the molecule 630 comprises two portions 632 and 634. The molecule 630 evidences a larger band gap state, with less π -delocalization. Application of an electric field causes charge separation in the molecule 630, resulting in a smaller band gap state, with better π -delocalization. Recombination of the charges returns the molecule 630 to its original state.

The following requirements must be met in this model:

(a) The molecule must have a modest dielectric constant ϵ_r and can be easily polarized by an external E-field, with ϵ_r in the range of 2 to 10 and polarization fields ranging from 0.01 to 10 V/nm;

5 (b) At least one segment of the molecule must have non-bonding electrons, or π -electrons, or π -electrons and non-bonding electrons that can be mobilized over the entire molecule or a part of the molecule;

(c) The molecule can be symmetrical or asymmetrical;

(d) The inducible dipole(s) of the molecule can be oriented in at least one di-
10 rection;

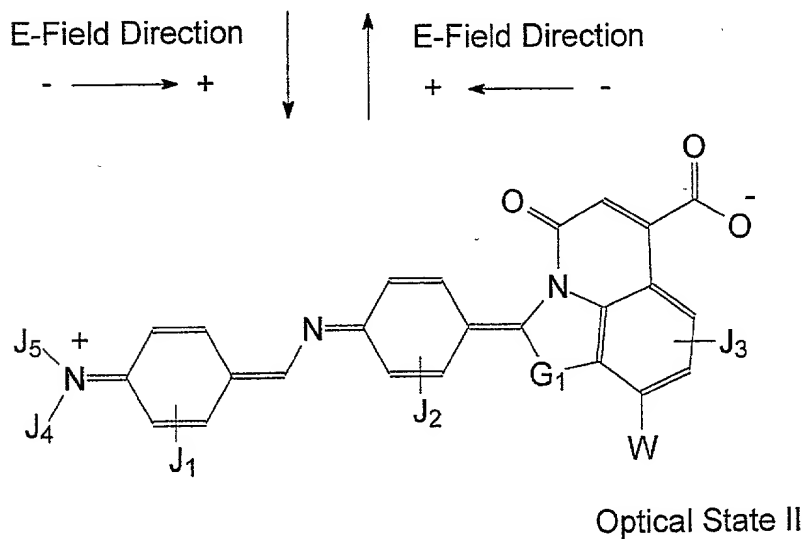
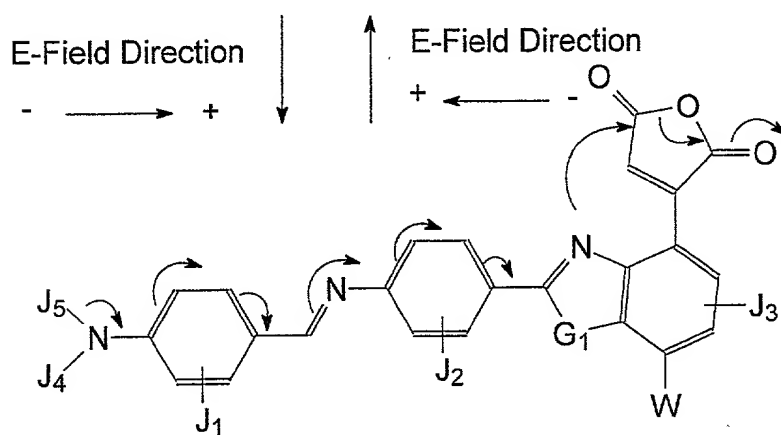
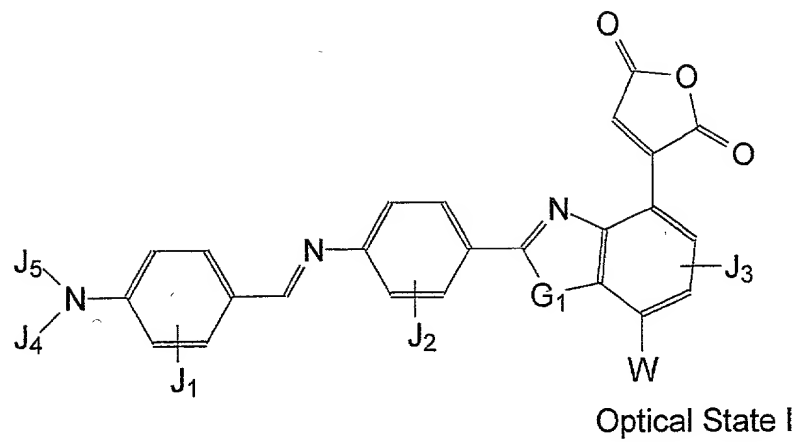
(e) The charges will be separated either partially or completely during E-field induced polarization;

(f) The states of charge separation or recombination can be E-field dependent or bi-stable, stabilized through inter- or intra-molecular forces such as covalent bond
15 formation, hydrogen bonding, charge attraction, Coulomb forces, metal complex, or Lewis acid (base) complex, etc.;

(g) The process of charge separation or recombination of the molecule can involve or not involve σ - and π -bond breakage or formation; and

(h) During the charge separation or re-combination process activated by an E-
20 field, the band gap of the molecule will change depending on the degree of the non-bonding electron, or π -electron, or π -electron and non-bonding electron delocalization in the molecule. Both optical and electrical properties of the molecules will be changed accordingly.

One example of an E-field induced band gap change (color change) via charge
25 separation or recombination involving bond breaking or bond formation is shown below (Example 3):



Example 3

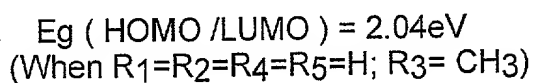
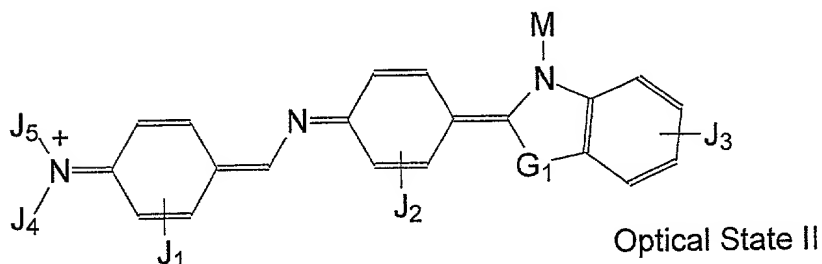
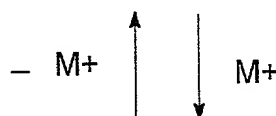
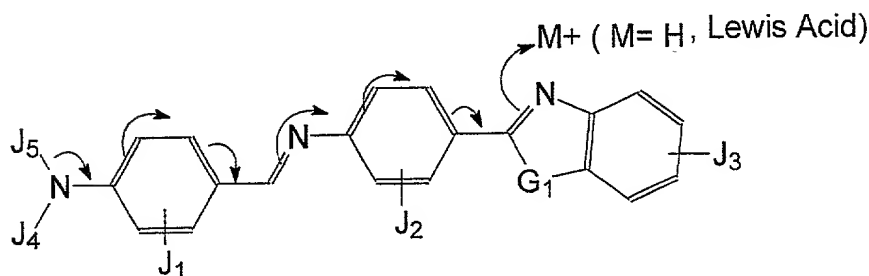
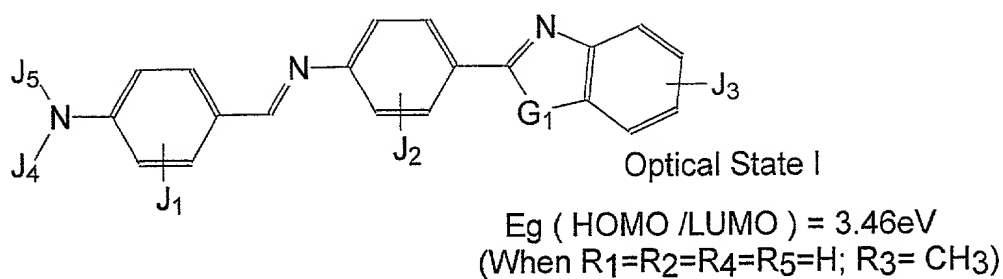
5 where:

The letters J₁, J₂, J₃, J₄ and J₅ represent tuning groups built into the molecule. The function of these tuning groups (e.g., OH, NHR, COOH, CN, nitro, etc.) is to provide an appropriate functional effect (e.g., both inductive effect and resonance effects) and/or steric effects. The functional effect is to tune the band gap ($\Delta E_{\text{HOMO/LUMO}}$) of the molecule to get the desired electronic as well as optical properties of the molecule. The steric effect is to tune the molecule conformation through steric hindrance, inter- or intra-molecular interaction forces (e.g., hydrogen bonding, Coulomb interaction, van der Waals forces) to provide bi- or multiple-stability of molecular orientation. They may be any one of the following: hydrogen, hetero atom (e.g., N, O, S, P, B, F, Cl, Br and I), functional group with at least one of above-mentioned hetero atoms, hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

The letter G₁ is a bridging group. The function of the bridging group is to connect two or more conjugated rings to achieve a desired chromophore. The bridging group may be any one of the following: hetero atoms (e.g., N, O, S, P, etc.) or functional group with at least one of above-mentioned hetero atoms (e.g., NH, etc.), hydrocarbon or substituted hydrocarbon.

The letter W is an electron-withdrawing group. The function of this group is to tune the reactivity of the maleic anhydride group of this molecule, which enables the molecule to undergo a smooth charge separation or recombination (bond breaking or formation, etc.) under the influence of an applied external E-field. The electron-withdrawing group may be any one of the following: carboxylic acid or its derivatives (e.g., ester or amide etc.), nitro, nitrile, ketone, aldehyde, sulfone, sulfuric acid or its derivatives, hetero atoms (e.g., F, Cl, etc.) or functional group with at least one of the hetero atoms (e.g., F, Cl, Br, N, O, S, etc.).

An example of an E-field induced band gap change involving the formation of a molecule-metal complex or a molecule-Lewis acid complex is shown below (Example 4):



Example 4

where:

- 5 The letters J_1 , J_2 , J_3 , J_4 and J_5 represent tuning groups built into the molecule. The function of these tuning groups (e.g., OH, NHR, COOH, CN, nitro, etc.) is to provide an appropriate functional effect (e.g. both inductive and resonance effects) and/or steric effects. The functional effect is to tune the band gap ($\Delta E_{HOMO/LUMO}$) of the molecule to get the desired electronic as well as optical properties of the molecule.
- 10 The steric effect is to tune the molecular conformation through steric hindrance, inter-

or intra-molecular interaction forces (e.g., hydrogen bonding, Coulomb interaction, van der Waals forces) to provide bi- or multiple-stability of the molecular orientation. They may be any one of the following: hydrogen, hetero atom (e.g., N, O, S, P, B, F, Cl, Br, and I), functional group with at least one of the above-mentioned hetero atoms, hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

The letter G_1 is a bridging group. The function of the bridging group is to connect two or more conjugated rings to achieve a desired chromophore. The bridging group may be any one of the following: hetero atoms (e.g., N, O, S, P, etc.) or functional group with at least one of above-mentioned hetero atoms (e.g., NH, etc.) or substituted hydrocarbon.

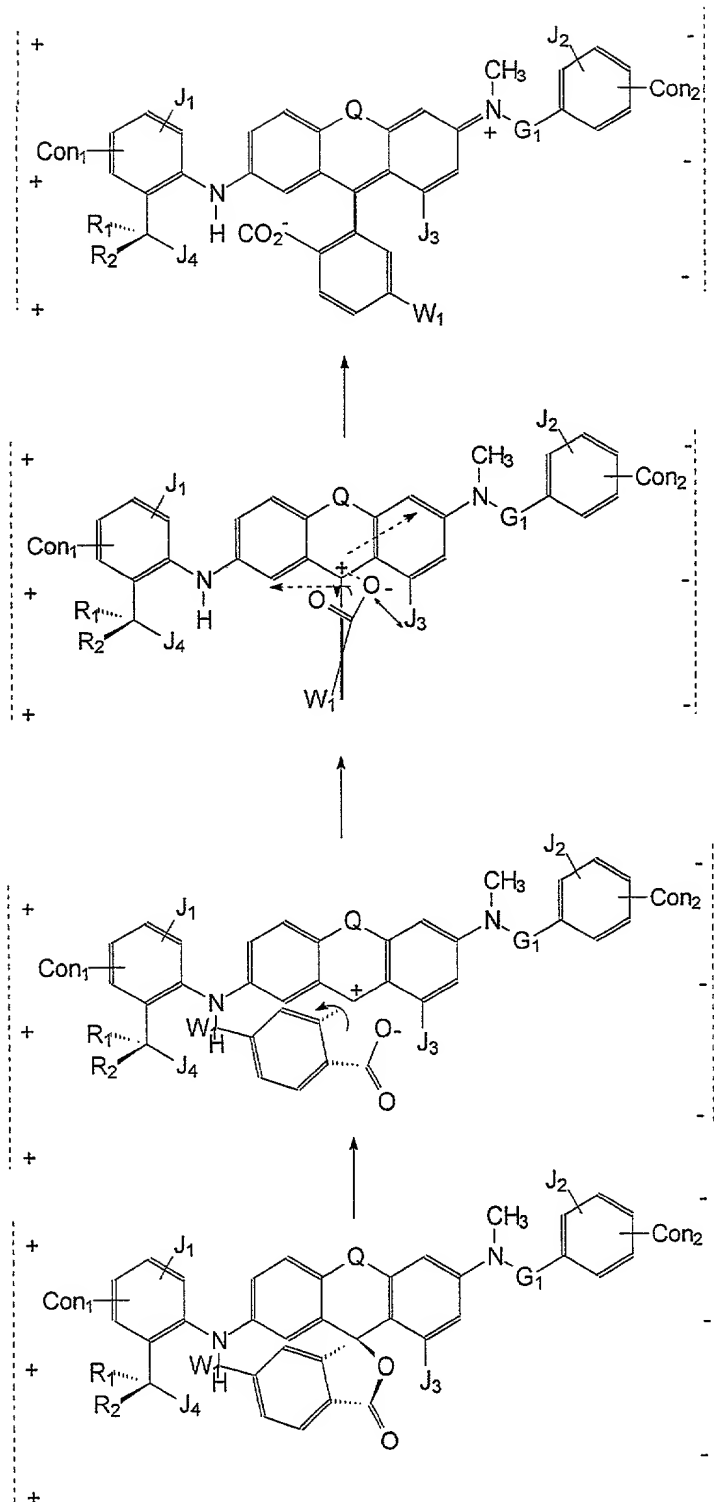
M^+ represents metals, including transition metals, or their halogen complexes or H^+ or other type of Lewis acid(s).

Model (2b): E-Field Induced Band Gap Change Caused by the Change of Extended Conjugation via Charge Separation or Recombination and π -Bond Breaking or Formation:

FIG. 6b is a schematic depiction of this model, which involves an E-field-induced band gap change caused by the change of extended conjugation via charge separation or recombination and π -bond breaking or formation. As shown in FIG. 6b, the molecule 630' comprises two portions 632' and 634'. The molecule 630' evidences a smaller band gap state. Application of an electric field causes breaking of the π -bond in the molecule 630', resulting in a larger band gap state. Reversal of the E-field re-connects the π -bond between the two portions 632' and 634' and returns the molecule 630' to its original state.

The requirements that must be met in this model are the same as listed for Model 2(a).

One example of an E-field induced band gap change cause by extended conjugation via charge separation (σ -bond breaking and π -bond formation) is shown below (Example 5):



Example 5

where:

The letter Q is used here to designate a connecting unit between two phenyl rings. It can be any one of following: S, O, NH, NR, hydrocarbon, or substituted hydrocarbon.

5 The letters Con₁ and Con₂ are connecting groups between one molecule and another molecule or between a molecule and a solid substrate (e.g., metal electrode, inorganic or organic substrate, etc.). They may be any one of the following: hydrogen (through a hydrogen bond), hetero atoms (i.e., N, O, S, P, etc.) or functional groups with at least one of above-mentioned hetero atoms (e.g., NH, etc.), hydrocarbons (ei-
10 ther saturated or unsaturated) or substituted hydrocarbons.

 The letters R₁ and R₂ represent spacing groups built into the molecule. The function of these spacer units is to provide an appropriate 3-dimensional scaffolding to allow the molecules to pack together while providing rotational space for each ro-
15 tor. They may be any one of the following: hydrogen, hydrocarbons (either saturated or unsaturated) or substituted hydrocarbons.

 The letters J₁, J₂, J₃ and J₄ represent tuning groups built into the molecule. The function of these tuning groups (e.g., OH, NHR, COOH, CN, nitro, etc.) is to provide an appropriate functional effect (e.g. both inductive and resonance effects) and/or steric effects. The functional effect is to tune the band gap ($\Delta E_{\text{HOMO/LUMO}}$) of the
20 molecule to get the desired electronic as well as optical properties of the molecule. The steric effect is to tune the molecular conformation through steric hindrance, inter- or intra-molecular interaction forces (e.g., hydrogen bonding, Coulomb interaction, van der Waals forces) to provide bi- or multiple-stability of molecular orientation. They may also be used as spacing group to provide an appropriate 3-dimensional
25 scaffolding to allow the molecules to pack together while providing rotational space for each rotor. They may be any one of the following: hydrogen, hetero atom (e.g., N, O, S, P, B, F, Cl, Br, and I), functional group with at least one of above-mentioned hetero atom, hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

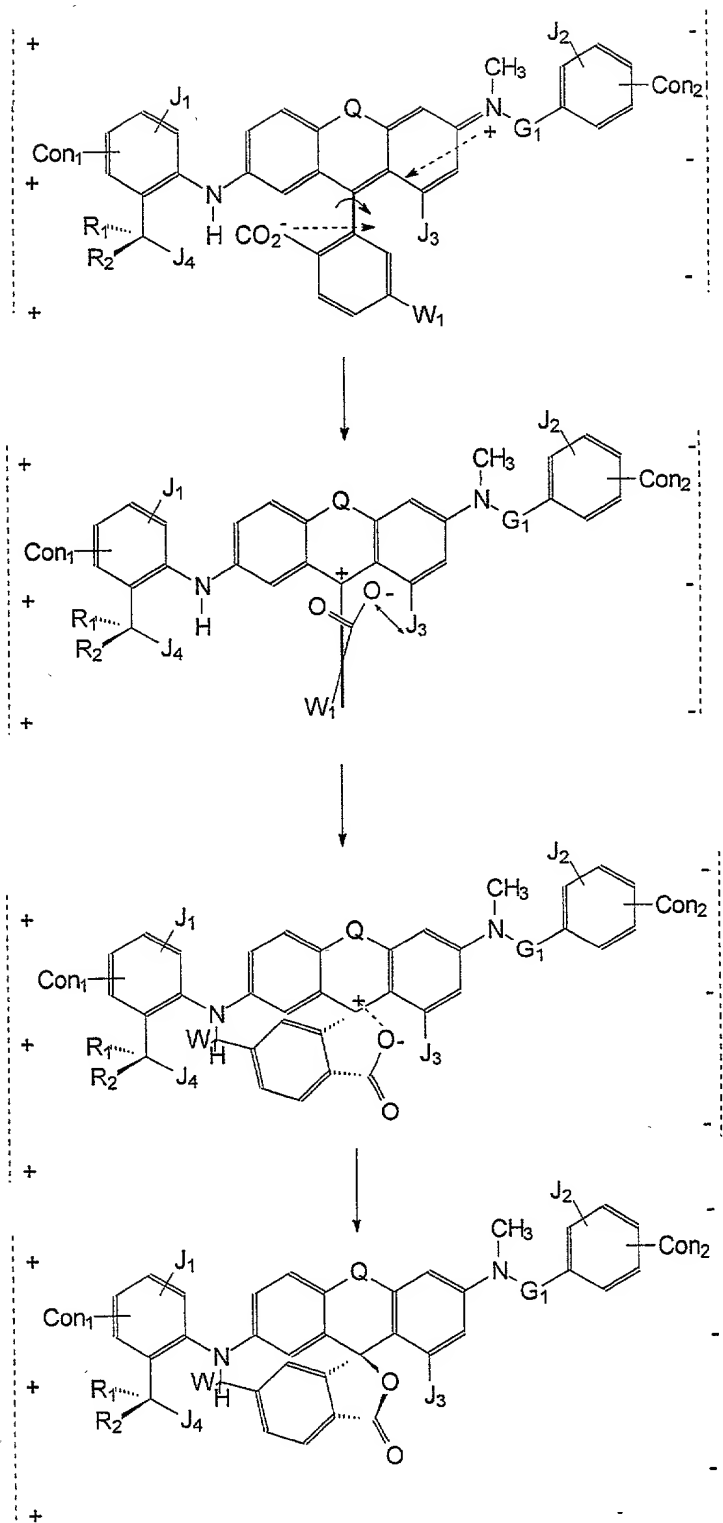
 The letter G₁ is a bridging group. The function of the bridging group is to con-
30 nect the stator and rotor or to connect two or more conjugated rings to achieve a desired chromophore. The bridging group may be any one of the following: hetero atoms (e.g., N, O, S, P, etc.) or functional groups with at least one of above-mentioned

hetero atoms (e.g., NH or NHHN, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

5 The letter W is an electron-withdrawing group. The function of this group is to tune the reactivity of the lactone group of this molecule, which enables the molecule to undergo a smooth charge separation or recombination (bond breaking or formation, etc.) under the influence of an applied external E-field. The electron-withdrawing group may be any one of the following: carboxylic acid or its derivatives (e.g., ester or amide etc.), nitro, nitrile, ketone, aldehyde, sulfone, sulfuric acid or its derivatives, hetero atoms (e.g., F, Cl, etc.) or functional group with at least one of hetero atoms
10 (e.g., F, Cl, Br, N, O and S, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

The uppermost molecular structure has a smaller band gap state than the lowermost molecular structure.

15 Another example of an E-field induced band gap change caused by breakage of extended π -bond conjugation via charge recombination and σ -bond formation is shown below (Example 6):



Example 6

where:

The letter Q is used here to designate a connecting unit between two phenyl rings. It can be any one of following: S, O, NH, NR, hydrocarbon, or substituted hydrocarbon.

5 The letters Con₁ and Con₂ are connecting groups between one molecule and another molecule or between a molecule and a solid substrate (e.g., metal electrode, inorganic or organic substrate, etc.). They may be any one of the following: hydrogen, hetero atoms (i.e., N, O, S, P, etc.) or functional group with at least one of above-mentioned hetero atoms (e.g., NH, etc.), hydrocarbon (either saturated or unsaturated)
10 or substituted hydrocarbon.

 The letters R₁ and R₂ represent spacing groups built into the molecule. The function of these spacer units is to provide an appropriate 3-dimensional scaffolding to allow the molecules to pack together while providing rotational space for each rotor. They may be any one of the following: hydrogen, hydrocarbon (either saturated or
15 unsaturated) or substituted hydrocarbon.

 The letters J₁, J₂, J₃ and J₄ represent tuning groups built into the molecule. The function of these tuning groups (e.g., OH, NHR, COOH, CN, nitro, etc.) is to provide an appropriate functional effect (e.g., both inductive and resonance effects) and/or steric effects. The functional effect is to tune the band gap ($\Delta E_{\text{HOMO/LUMO}}$) of the
20 molecule to get the desired electronic as well as optical properties of the molecule. The steric effect is to tune the molecule conformation through steric hindrance, inter- or intra-molecular interaction forces (e.g. hydrogen bonding, Coulomb interaction, van der Waals forces) to provide bi- or multiple-stability of molecular orientation. They may also be used as spacing groups to provide an appropriate 3-dimensional
25 scaffolding to allow the molecules to pack together while providing rotational space for each rotor. They may be any one of the following: hydrogen, hetero atom (e.g., N, O, S, P, B, F, Cl, Br, and I), functional groups with at least one of above-mentioned hetero atom, hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

 The letter G₁ is a bridging group. The function of this bridging group is to
30 connect stator and rotor or to connect two or more conjugated rings to achieve a desired chromophore. The bridging group may be any one of the following: hetero atoms (e.g., N, O, S, P, etc.) or functional group with at least one of above-mentioned

hetero atoms (e.g., NH or NHNH, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

The letter W is an electron-withdrawing group. The function of this group is to tune the reactivity of the lactone group of this molecule, which enables the molecule to undergo a smooth charge separation or recombination (bond breaking or formation, etc.) under the influence of an applied external E-field. The electron-withdrawing group may be any one of the following: carboxylic acid or its derivatives (e.g., ester or amide, etc.), nitro, nitrile, ketone, aldehyde, sulfone, sulfuric acid or its derivatives, hetero atoms (e.g., F, Cl etc.) or functional group with at least one of hetero atoms (e.g., F, Cl, Br, N, O, S, etc.), hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

Again, the uppermost molecular structure has a smaller band gap state than the lowermost molecular structure.

The present invention turns ink or dye molecules into active devices that can be switched with an external electric field by a mechanism completely different from any previously described electro-chromic or chromogenic material. The general idea is to use modified Crystal Violet lactone type of molecules in which the C-O bond of the lactone is sufficiently labile enough and can undergo a bond breaking and forming (see Examples 5 and 6 above) under the influence of an applied electric field.

A positive and a negative charge are generated during the C-O bond breaking process. The resulting charges will be separated and move in opposite directions parallel to the applied external field (upper part of the molecule), or bond rotation (lower part of the molecule). The two aromatic rings with an extended dipole (upper part and lower part) of the molecule is completely conjugated, and a color (red-shift) results (see Example 5). However, the molecule is designed to have inter- and/or intra-molecular forces, such as hydrogen bonding, Coulomb, or dipole-dipole interactions as well as steric repulsions, or by a permanent external E-field to stabilize both charges in this particular orientation. Thus, a large field is required to unlatch the molecule from its initial orientation. Once switched into a particular orientation, the molecule will remain in that orientation until it is switched out.

When a reverse E-field is applied (Example 6), both charges tend to realign themselves to the direction of the reverse external field. The positive charge on the

upper part of the molecule will migrate to the center part of the molecule (tri-aryl methane position) from the side of the molecule through the non-bonding electron, or π -electron, or π -electron and non-bonding electron delocalization. Likewise, the negative charged lower part of the molecule will tend to move closer to the external E-field through C-C bond rotation. A key component of the molecule design is that there is a steric and static repulsion between the CO_2^- and the J_3 and J_4 groups that will prevent the lower part of the molecule (the negative charged sector) from rotating through a complete 180 degree half cycle. Instead, the rotation is halted by the steric interaction of bulky groups on the lower part and the upper part at an angle of approximately 90 degrees from the initial orientation. Furthermore, this 90 degree orientation is stabilized by a C-O bond formation and charge recombination. During this process, a tetrahedral carbon (an isolator) is formed at the tri-aryl methane position. The conjugation of the molecule is broken and the HOMO and LUMO are no longer delocalized over the entire upper part of the molecule. This has the effect of shrinking the size of the volume occupied by the electrons, which causes the HOMO-LUMO gap to increase. A blue-shifted color or transparent state will result during this process.

For colored ink and dye molecules, the limitation of the positive charge migration just between one side of a molecule and the center position is crucial. Another important factor is the ability to switch the rotor (lower part of molecule) between two states separated by an optically significant angle (nominally 10 to 170 degrees) from the stators (the upper part of the molecule). When the intra-molecular charge separation reaches a maximum distance, then the upper most part of the molecule becomes completely conjugated. Thus, the π -electrons or π -electrons and non-bonding electrons of the molecule, through its highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), are delocalized over the upper most region. The effect is identical to that for a quantum mechanical particle in a box: when the box is the size of the entire molecule, i.e., when the orbitals are delocalized, then the gap between the HOMO and LUMO is relatively small. In this case, the HOMO-LUMO gap of the molecule is designed to yield the desired color of the ink or dye. The HOMO-LUMO gap for the all-parallel structure can be tuned by substituting various chemical groups (J_1 , J_2 , J_3 , J_4 , and W) onto the different aromatic rings of the

molecule. In the case where the rotor (lower part of the molecule) is rotated by 10 to 170 degrees with respect to the stators (the upper part of the molecule), depending on the nature of the chemical substituents (J_1 , J_2 , J_3 , J_4 , and W) bonded to the rotor and stator, then the increased HOMO-LUMO gap will correspond to a color that is blue-shifted with respect to the color of the all-parallel structure. With sufficient shifting, the molecule becomes transparent, if the new HOMO-LUMO gap is large enough. Thus, the molecule is switchable between two colors or from one color to a transparent state.

Examples 5 and 6 show two different states of a representative switchable molecule under the influence of an externally applied E-field. For this particular type of molecule, a sufficiently thick molecular film is grown, for example using Langmuir-Blodgett techniques, vapor phase deposition, or electrochemical deposition, such that the orientation axis of the molecules is perpendicular to the plane of the electrodes used to switch the molecules. Another deposition technique is to suspend the molecule as a monomer/oligomer or solvent-based solution that is thick film coated (e.g., reverse roll) or spin-coated onto the substrate and subsequently polymerized (e.g., by UV radiation) or dried while the coating is subjected to an electric field that orients the molecule. A top electrode may be a transparent conductor, such as indium-tin oxide, and the films are grown such that the molecular axis is parallel to the plane of the electrodes. The molecules form solid-state or liquid crystals in which the large stator groups are locked into position by intermolecular interactions or direct bonding to a support structure, but the rotor is small enough to move within the lattice of the molecules.

25 Model (3): E-Field Induced Band Gap Change via Molecular Folding or Stretching

FIG. 7 is a schematic depiction of this model, which involves an E-field-induced band gap change caused by the change of extended conjugation via molecular folding or stretching. As shown in FIG. 7, the molecule 730 comprises three portions 732, 734, and 736. The molecule 730 evidences a smaller band gap state due to an extended conjugation through a large region of the molecule. Application of an electric field causes breaking of the conjugation in the molecule 730, due to molecular folding about the central portion 734, resulting in a larger band gap state due to the

non-extended conjugation in the large region of the molecule. Reversal of the E-field unfolds the molecule 730 and returns the molecule to its original state. Stretching and relaxing of the central portion 734 of the molecule 730 has the same effect.

The following requirements must be met in this Model:

5

(a) The molecule must have at least two segments;

(b) Several segments (portions) should have non-bonding electrons, or π -electrons, or π -electrons and non-bonding electrons involved in the HOMOs, LUMOs, and nearby orbitals;

10

(c) The molecule may be either symmetrical or asymmetrical with a donor group on one side and an acceptor group on another side;

(d) At least two segments of the molecule have some functional groups that will help to stabilize both states of folding and stretching through intra- or inter-molecular forces such as hydrogen bonding, van der Waals forces, Coulomb attraction or metal complex formation;

15

(e) The folding or stretching states of the molecule must be E-field addressable;

20

(f) In at least one state (presumably in a fully stretched state), the non-bonding electrons, or π -electrons, or π -electrons and non-bonding electrons of the molecule will be well-delocalized, and the π - and p-electrons electrons of the molecule will be localized or only partially delocalized in other state(s);

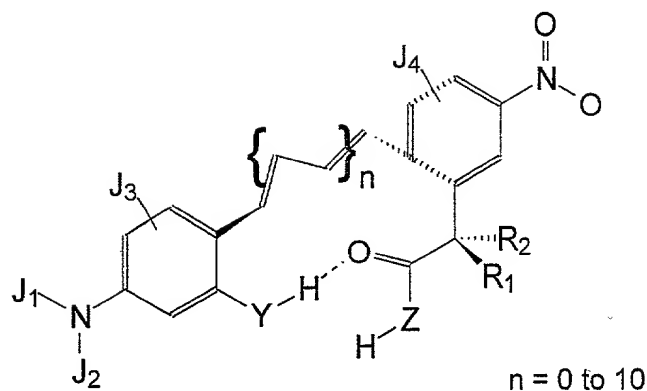
25

(g) The band gap of the molecules will change depending on the degree of non-bonding electron, or π -electron, or π -electron and non-bonding electron delocalization while the molecule is folded or stretched by an applied external E-field, and this type of change will also affect the electrical or optical properties of the molecule as well; and

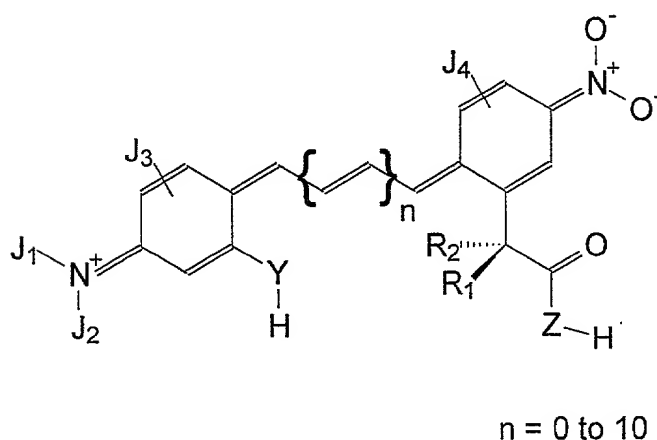
(h) This characteristic can be applied to these types of molecules for optical or electrical switches, gates, storage or display applications.

An example of an E-field induced band gap change via molecular folding or stretching is shown below (Example 7):

30



Molecule Folding \rightleftharpoons Stretching Out



Example 7

5 where:

The letters R_1 and R_2 represent spacing groups built into the molecule. They may be any one of the following: hydrogen, hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

10 The letters J_1 , J_2 , J_3 , J_4 and J_5 represent tuning groups built into the molecule. The function of these tuning groups (e.g., OH, NHR, COOH, CN, nitro, etc.) is used to provide an appropriate functional effect (e.g., both inductive and resonance effects) and/or steric effects. The functional effect is to tune the band gap ($\Delta E_{\text{HOMO/LUMO}}$) of the molecule to get the desired electronic as well as optical properties of the molecule. The steric effect is to tune the molecular conformation through steric hindrance, inter-

or intra-molecular interaction forces (e.g. hydrogen bonding, Coulomb interaction, van der Waals forces) to provide bi- or multiple-stability of molecular orientation. They may also be used as spacing group. They may be any one of the following: hydrogen, hetero atom (e.g., N, O, S, P, B, F, Cl, Br and I), functional group with at least one of above-mentioned hetero atom, hydrocarbon (either saturated or unsaturated) or substituted hydrocarbon.

Letters Y and Z are functional groups that will form inter- or intra-molecular hydrogen bonding. They may be any one of following: SH, OH, amine, hydrocarbon, or substituted hydrocarbon.

The molecule on the top of the graphic has a larger band gap due to the localized conjugation various parts of the molecule, while the molecule on the bottom has a smaller band gap due to an extended conjugation through a large region of the molecule.

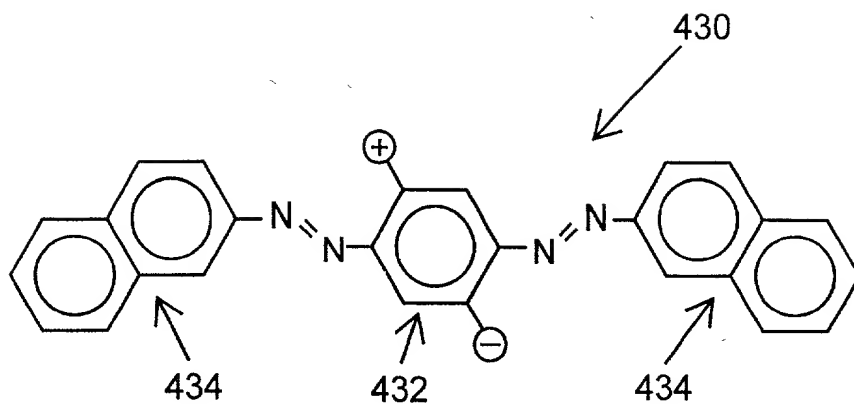


FIG. 5a

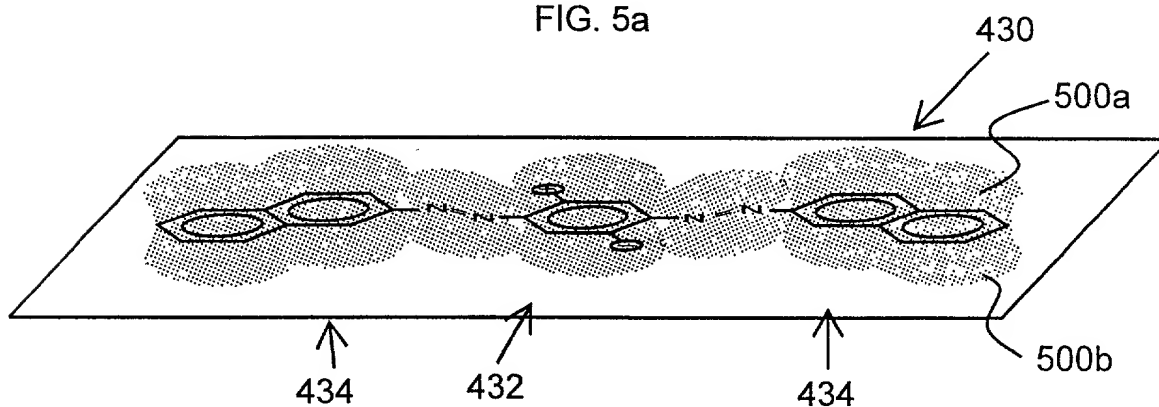


FIG. 5b

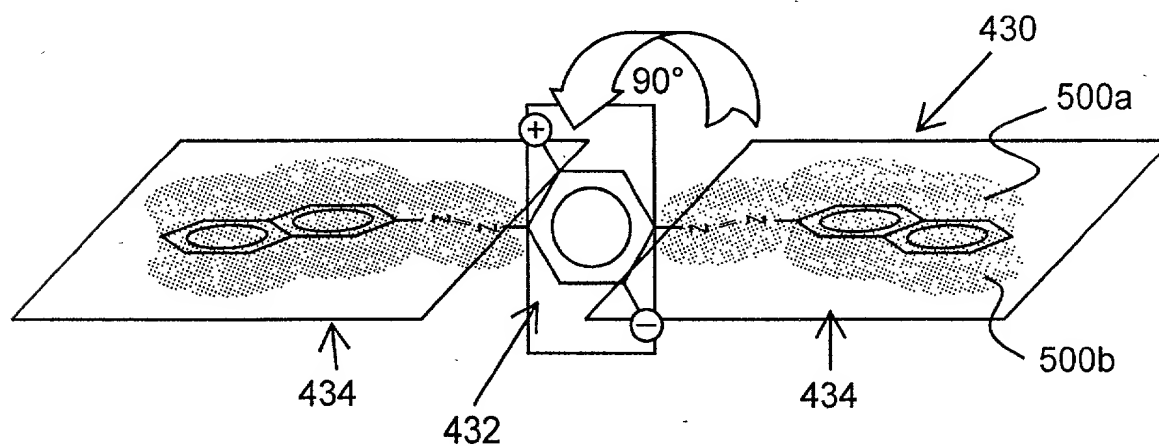


FIG. 5c

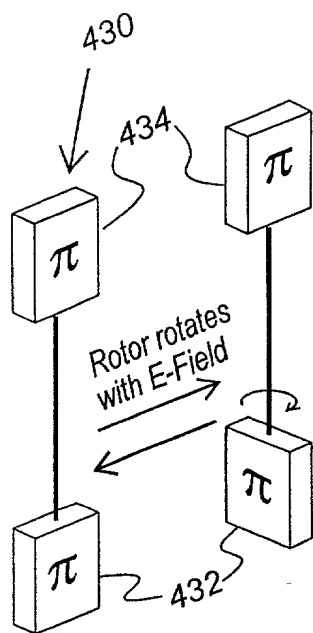


FIG. 4

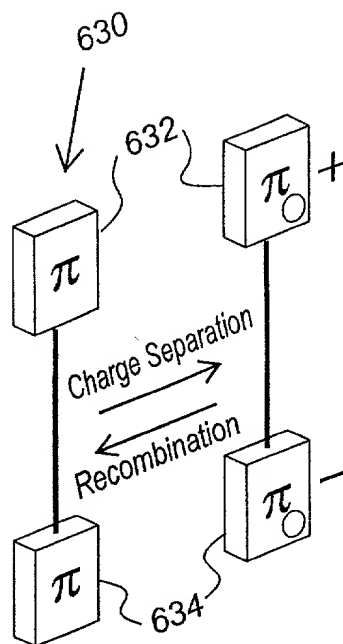


FIG. 6a

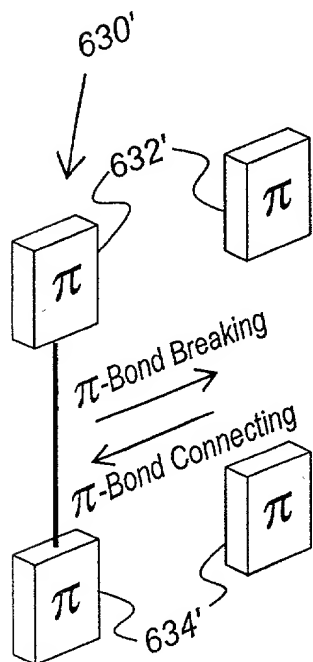


FIG. 6b

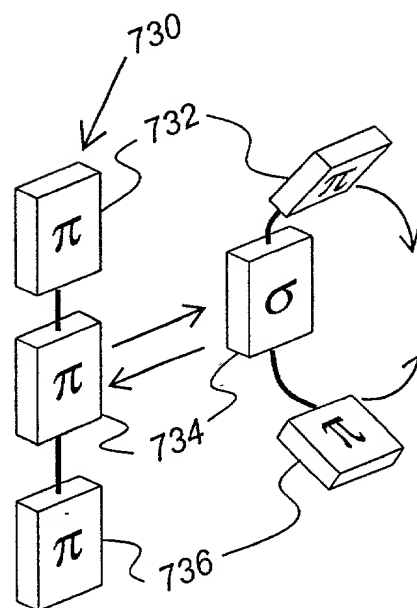


FIG. 7